Bioresource Technology 101 (2010) 5222–5228

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Properties of dairy-manure-derived biochar pertinent to its potential use in remediation

Xinde Cao [a,*], Willie Harris [b]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA

ARTICLE INFO

Article history:
Received 5 January 2009
Received in revised form 8 February 2010
Accepted 8 February 2010
Available online 4 March 2010

Keywords:
Dairy manure
Waste management
Biochar
Environmental remediation

ABSTRACT

Conversion of waste products into biochar (BC) is being considered as one of several waste disposal and recycling options. In this study, we produced BC from dairy manures by heating at low temperatures ($\leqslant$500 °C) and under abundant air condition. The resultant BC was characterized for physical, chemical, and mineralogical properties specifically related to its potential use in remediation. The BC from all manures behaved similarly. Surface area, ash content, and pH of the BC increased as temperature increased, while yield decreased with increasing temperature. The BC was rich in mineral elements such as N, Ca, Mg, and P in addition to C, and concentrations of C and N decreased with increasing temperature as a result of combustion and volatilization; while P, Ca, and Mg increased as temperature increased. For example, C significantly decreased from 36.8% at 100 °C to 1.67% at 500 °C; whereas P increased from 0.91% to 2.66%. Water soluble P, Ca, and Mg increased when heated to 200 °C but decreased at higher temperatures likely due to increased crystallization of Ca–Mg–P, as supported by the formation of whitlockite $(Ca,Mg)_3(PO_4)_2$ following 500 °C treatment. The presence of whitlockite was evidenced by X-ray diffraction analysis. Quartz and calcite were present in all BC produced. The BC showed appreciable capability of adsorption for Pb and atrazine from aqueous solution, with Pb and atrazine removal by as high as 100% and 77%, respectively. The results indicated that dairy manure can be converted into biochar as an effective adsorbent for application in environmental remediation.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Approximately 350 billion pounds of dry manure are produced annually in the United States (Koneswaran and Nierenberg, 2008). Since manure is rich in nutrients, e.g., N and P, land application of the manure to fertilize soil has been a common method for managing dairy manure in the US (Harris et al., 2008). However, many agricultural fields that have received long-term manure applications have high risks of runoff and leaching of manure-derived components such as N and P (Zhang et al., 2006), such that water quality of streams and lakes can be threatened (Sharpley et al., 2000). This has resulted in more strict environmental regulations towards the management of dairy manure. Therefore, developing environmentally beneficial uses for manure would help to alleviate manure waste management problems.

Agricultural crop waste products (e.g., sugar cane bagasse, soybean hulls and various nutshells) have been extensively evaluated as precursors to activated carbon (AC) (Toles et al., 1997; Johns et al., 1998; Ahmedna et al., 2000; Marshall et al., 2000; Ng et al., 2002). The crop residues are pyrolyzed at high temperature (greater than 500 °C) and under oxygen-free condition, followed by various activation processes to form AC (Johns et al., 1998). In general, AC is characterized by a high surface area which imparts a high adsorption affinity for metal- and organic contaminants (Toles et al., 1997; Johns et al., 1998). Recently, studies have been conducted on turning animal waste (e.g., poultry manure, broiler manure, and turkey manure) into AC for remediation applications (Lima and Marshall, 2005a,b, and c). Lima and Marshall (2005a) pyrolyzed broiler litter and cake at 700 °C followed by steam activation in an inert atmosphere, producing 18–28% AC with surface area ranging from 253 to 548 $m^2\ g^{-1}$. The broiler cake-based AC exhibited a high affinity for Cu (adsorption capacity of up to 1.92 $mmol\ g^{-1}\ C^{-1}$). Further work indicated that turkey manure-derived AC has similar yield and surface area to the AC produced from broiler waste and showed a considerable potential to remove Cu from water (Lima and Marshall, 2005b). In another experiment, the poultry manure-based AC was shown to adsorb Cd and Zn in addition to Cu (Lima and Marshall, 2005b).

Turning abundant, agricultural waste products (e.g., crop residues, animal manure) into materials such as AC that can absorb contaminants can have environmental implications for improving

---

* Corresponding author. Tel.: +86 21 3420 2841; fax: +86 21 5474 0825.
E-mail address: xdcao@sjtu.edu.cn (X. Cao).

0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.02.052

waste management and protecting the environment. However, few studies have been conducted on low temperature (typically less than 500 °C) conversion of animal wastes into carbon-rich residues and on efficacy of these residues for environmental mitigation (Shinogi et al., 2003; Shinogi and Kanri, 2003; Martins et al., 2007). Low temperature conversion generally produces the charred residue of incompletely combusted organic materials which has been referred to as "biochar" (BC) (Lehmann, 2007a,b). Biochar requires less energy and cost to produce than AC generation since BC is generally obtained at lower temperature and without further activation processing (Shinogi et al., 2003; Lehmann, 2007b). Biochar has a relatively structured carbon matrix with a medium-to-high surface area, suggesting that it may act as a surface sorbent which is similar in some aspects to AC. It has been proven that BC is effective in adsorbing organic pollutants from waste water (Lehmann et al., 2006); it can also improve soil fertility and increase crop production (Lehmann, 2007a; Liang et al., 2006). Application of BC to soil was recently proposed as a novel approach to establish a significant, long-term, sink for atmospheric CO_2 in terrestrial ecosystems (Renner, 2007; Lehmann, 2007b).

In the present study, we converted dairy manure into BC by heating at low temperatures ($\leqslant$500 °C) and without air excluded in views of production cost and for its prospective use as an environmental amendment. The procedure used was different from pyrolysis treatment with absence of oxygen, a typical process of production for bioenergy along with BC. The BC produced at different temperatures was compared for the physico-chemical properties such as yield, ash content, specific surface area, elements, pH, and mineral components. Remediation application of the BC in sorption of contaminants from aqueous solutions was also evaluated.

2. Methods

2.1. Dairy manure and heat treatment

Four dairy manure solids (M-1, M-2, M-3, and M-4) were collected from three Florida dairies. Samples M-1 and M-4 were obtained at different times from the same North-Central Florida dairy (St. Johns River watershed); M-2 was from another North-Central Florida dairy (Suwannee River watershed); and M-3 was from a South-Florida dairy. Manures were air-dried and ground to less than 1 mm. The ground manures were then put in a glass beaker and heated in an Isotemp® Muffle Furnace (Thermo Fisher Scientific, Inc., Pittsburgh, PA, USA).

The heated air was not controlled and a hole in the top of the furnace served to vent gasses from combustion of the manure during heating. Temperature was raised to the selected values at a speed of approximately 25 °C min^{-1} and held for 4 h. After 4 h of heating, the furnace was turned off and the sample was allowed to cool to room temperature. Each of manure was heated with three replicates. Carbonization extent of the biomass is strongly dependent on production temperature (Bergman and Kiel, 2005). The residue produced at 100 °C is merely drying of manure with some minor modifications of the organic structure. Heating at 200 °C is at torrefaction where the biomass becomes completely dried and hemicellulose is limitedly devolatilized and carbonized (Bergman and Kiel, 2005). Samples heated at 350 °C undergo incomplete combustion, producing a carbon-rich char. Heating at 500 °C may result in complete combustion of C in the presence of air and mainly ash may remain (minimal BC). However, for consistency, residues produced at 100, 200, 350, and 500 °C were labeled as BC100, BC200, BC350, and BC500, respectively, where the number following BC indicated the final production temperature. All the BCs were then directly subjected to physical and chemical characterization without any further treatment. For the comparison, the original manure dried at room temperature 25 °C (referred to as BC25) was included. The BC yield was calculated using the equation: Yield (%) = (MWa/MWb) × 100, where MWa and MWb designate weights of manure after and before heating, respectively.

2.2. Physical and chemical properties of the BCs

Total C and N analyses were conducted on a solid TC/TN analyser (TOC-V/SSM-5000; Shimadzu Co. Ltd., Kyoto, Japan). Other elements (P, Ca, and Mg) were determined using the USEPA method 3050B (USEPA, 1986). Ash content was measured by heating the samples at 1000 °C for 2 h and calculated using equation: Ash (%) = (BWa/BWb) × 100, where BWa and BWb designate weights of BC after and before heating, respectively. The specific surface areas (SSA) were measured with N_2 adsorption at 77 K determined by a NOVA-2000 surface area analyser (QuantaChrome Co., Boynton Beach, FL, USA). All samples were out-gassed at 105 °C for 16 h before N_2 sorption. The multipoint Brunauer–Emmett–Teller method was employed to calculate surface area. Four data points, with relative pressures of 0.05–0.3, were used to construct the monolayer adsorption capacity.

The pH of BC was determined in a mixture of 5 g BC and 10 mL de-ionized water following 1-h equilibrium. Water soluble P, Ca, Mg, and NH_4^+–N were extracted by mixing 5 g BC with 50 mL de-ionized H_2O. After being shaken on a reciprocal shaker for 1 h, the mixture was centrifuged at 11,000g for 20 min. The supernatant was filtered through a 0.45-μm pore-size Millipore filter. The filtrate was acidified to pH less than 2 with HNO_3 prior to Ca and Mg analysis using atomic absorption spectrometry (AAS) (Varian 220FS, Varian, Walnut Creek, CA, USA). Phosphorus concentration was determined by colorimetry using the molybdate/ascorbic acid method (Olsen and Sommers, 1982). NH_4–N was determined colorimetrically using EPA Methods 350.1.

2.3. Characterization of the BC solid phases

The BC produced from the M-3 manure sample was characterized using X-ray diffraction (XRD), infrared (IR) spectroscopy, and thermogravimetry (TG). The XRD analysis was conducted on a computer-controlled diffractometer equipped with stepping motor and graphite crystal monochromator (Model I-2 manufactured by Nicolet, Madison, WI, USA). Samples were mounted for XRD as a powder on a quartz crystal specially cut to minimize background. The diffractometer was operated at 35 kV and 20 mA and data collected over the 2θ range from 5 to 50° using Cu $K\alpha$ radiation with a scan speed of 1° per minute. Identification of phase peaks was accomplished by comparing the observed XRD patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS, 1980).

Infrared spectra were obtained for the same samples characterized by XRD using Thermo Fisher (Nicolet) Magna 760 with SpectraTech Gemini diffuse reflectance attachment (Thermo Fisher Scientific, Inc., Waltham, MA, USA). Spectra were collected in the range of 400–4000 cm^{-1} at 4 cm^{-1} resolution and 64 scans per sample. Samples were prepared as KBr pellets by mixing samples with KBr at 1.3–1.5 wt% for 20 s using a Wig-L-Bug ball mill. All sample spectra were corrected for water vapor and carbon dioxide and an 11 point moving average smoothing algorithm was applied prior to peak analysis. Since BC samples were much blacker, much finer, and gave only negative peaks, an inverse was done on BC samples.

Thermogravimetry was conducted using a computer-controlled thermogravimetric analyser (DuPont Instrument Co., Wilmington, DE, USA). The BC samples were heated from 25 to 1000 °C at a rate of 20 °C per min. Weight losses attributable to mineral reactions that produced volatile reaction products (H_2O, CO_2) at specified temperature ranges were used diagnostically to corroborate XRD identification of minerals. Quantitative mass loss was used to determine organic matter loss via combustion and calcite ($CaCO_3$) mass percent based on the stoichiometry of its decomposition reaction.

2.4. Sorption of the BC for environmental contaminants

The purpose was to determine potential of BC for sorption of heavy metal and/or organic contaminants for aqueous solutions. Atrazine and Pb were chosen as model organic and heavy metal contaminant, respectively. The sorption experiment was conducted in 60-mL polypropylene tubes by mixing 0.25 g of BC (M-3 derived BC chosen) with 50 mL of 0.01 M $NaNO_3$ containing 207 mg L^{-1} Pb and 10 mg L^{-1} atrazine. NaN_3 was added into the solution at 200 mg L^{-1} to inhibit microbial degradation. After the mixture was shaken for 4 d at a speed of 60 rpm, solid and liquid phases were separated by centrifugation at 4000 rpm for 15 min and the liquid solution was filtered through 0.22-μm Millipore filter. The filtrate was analysed for Pb and atrazine concentrations using AAS and HPLC, respectively (Cao et al., 2009). Sorption of Pb and atrazine was calculated from the difference between initial and final solution concentrations.

2.5. Statistic analysis

All results were expressed as an average of three replicates with standard deviation if not stated, and temperature effects determined by analysis of variance using the general linear model procedure of the Statistical Analysis System (SAS Institute Inc.). Differences among the temperatures were separated by least significant difference, at the 0.05 probability level.

3. Results and discussion

3.1. BC yield and ash content

Changes in yield and ash of the BC produced at different temperatures are shown in Fig. 1a and b. The BC yield was reduced for all manures with increased temperature (Fig. 1a). A large decrease in yield occurred between 100 and 350 °C, agreeing with the observation of Shinogi and Kanri (2003) who indicated a significant decrease of yield between 200 and 400 °C for bagasse, rice husk, and cow biosolid likely due to the destruction of cellulose and hemicellulose. Sumiyaki Association (1991) reported that cellulose abruptly loses mass around 180–250 °C, while lignin loses mass almost linearly with temperature. A slight yield decrease between 350 and 500 °C is likely attributable to complete combustion of organic matter at temperatures higher than 350 °C.

The ash content of BC for all four manures increased with temperature used for the production (Fig. 1b). The temperature trend for ash content was similar to that produced from other agricultural wastes such as bagasse, rice husk, and cow biosolid (Shinogi and Kanri, 2003). However, the manure-derived BC ash was much higher (up to 96%, Fig. 1b) than those wastes (up to 60%; Shinogi and Kanri, 2003), probably due to the presence of minerals such as calcite and quartz in the manure (described in the following section). The increase in ash from 25 to 500 °C resulted from progressive concentration of minerals and organic matter combustion residues as temperature increased. More than 95% ash in the BC

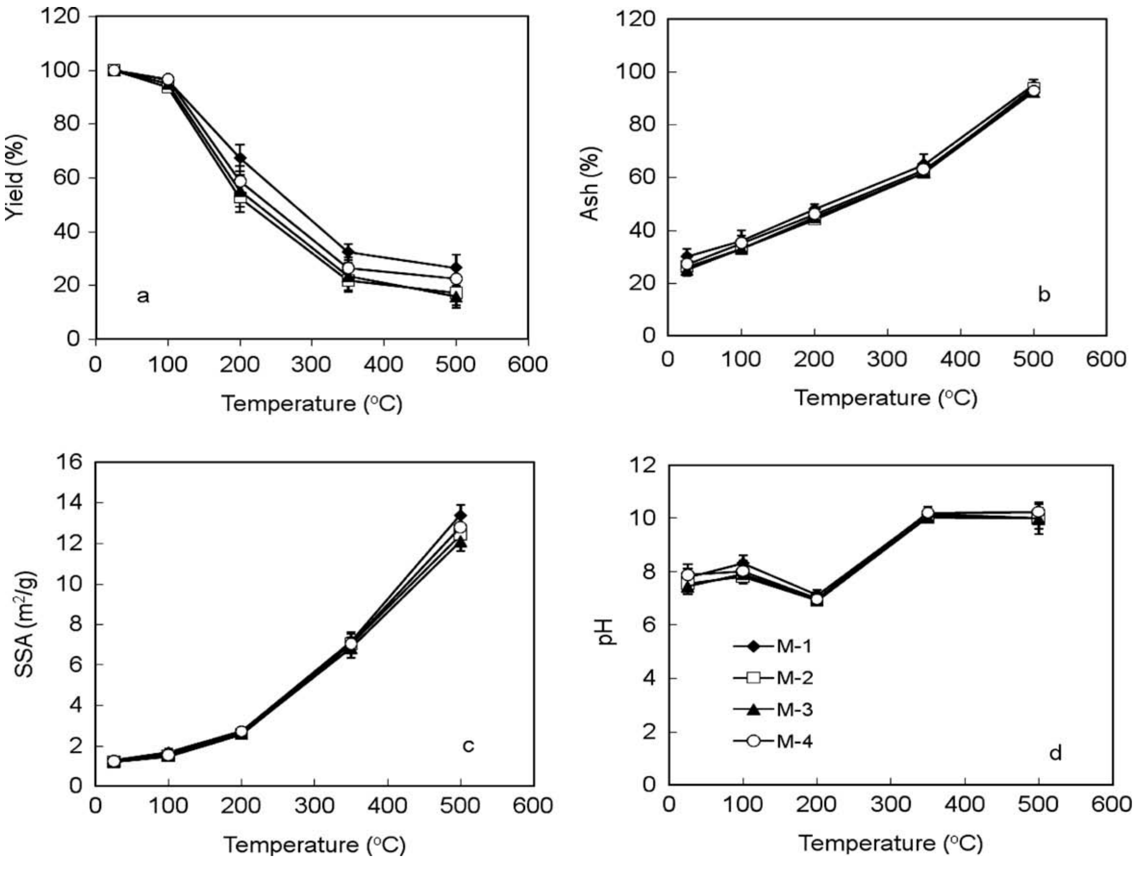

Fig. 1. Change in yield (a), ash (b), specific surface area (c), and pH (d) of all four original manures and manure-derived biochar as a function of production temperatures.

produced at 500 °C may be attributed to the complete combustion of C, indicating that the BC produced at 500 °C was almost all ash.

3.2. SSA and pH

The SSA of BC increased for all four manures with increasing temperature (Fig. 1c), especially between 200 °C (approximately 2.7 $m^2\ g^{-1}$) and 500 °C (approximately 13 $m^2\ g^{-1}$). The SSA range was within that of rice husk, eucalyptus sawdust, activated sludge, and cow biosolids treated by pyrolysis process (Shinogi and Kanri, 2003; Martins et al., 2007), but much smaller than that (100–1000 $m^2\ g^{-1}$) of plant residue such as wood charcoal, sugarcane bagasse, wheat residue, or AC (Shinogi and Kanri, 2003; Chun et al., 2004; Lima and Marshall, 2005a). It seems that the parent biomass composition rather than BC production procedure mainly determined the SSA of BC. The dairy manure, rice husk, eucalyptus sawdust, activated sludge, and cow biosolids may contain mineral components; for example, the dairy manure is rich in calcite, quartz, etc (shown in the following section) and rice husk contains silicon (Martins et al., 2007). Both pyrolysis process in absence of oxygen and heat treatment in presence of oxygen produced BC with less SSA. However, plant residues such as wood charcoal, sugarcane bagasse, wheat residue, or AC are abundant in organic C which could produce higher porosity when heated, resulting in BC with high SSA (Martins et al., 2007). Also, BC produced in the present study did not receive further acid activation treatment which tends to increase SSA (Chun et al., 2004; Lima and Marshall, 2005a). Surface area is one of the important parameters to evaluate absorption, especially for organic molecules (Shinogi and Kanri, 2003). Such a low surface area for the dairy manure-derived BC precludes it being a viable substitute for AC as a surface absorbent. For such applications, surface areas in the 400–1000 $m^2\ g^{-1}$ are typical, with larger interfacial pore distribution (Shinogi and Kanri, 2003).

All four manures exhibited the same pH trend via production temperature. The untreated manures (25 °C) were alkaline (pH approximately 7.5–8). The pH increased with temperature with the exception of the 200 °C treatment which showed a pH reduction to approximately 7 (Fig. 1d). Abe et al. (1998) indicated that cellulose and hemicellulose could be decomposed around 200–300 °C, producing organic acids and phenolic substances that lowered pH of the products. Beyond 300 °C, the C started to become ashed and alkali salts began to separate from the organic matrix, increasing the BC pH to above 10. After all the alkali salts were “leached” from the pyrolytic structure (Shinogi and Kanri, 2003), the pH became constant at 350 and 500 °C (Fig. 1d). Higher pH at 350 and 500 °C indicate their potentials as amendments to neutralize soil acidity (Abe, 1988).

3.3. Elemental analysis

Elemental composition was similar for all manure-derived BC (Table 1). The BC contained high concentrations of C and N, and their concentrations significantly decreased with increasing production temperature. For example, average C and N were reduced from 31.1% and 2.98%, respectively at 200 °C to 1.67% and 0.04% at 500 °C (Table 1). The decrease of C and N resulted from the increasing biomass combustion and organic volatilization with increasing temperature. In addition to C and N, the BC was abundant in mineral elements such as P, Ca and Mg (Table 1). Richness of P, Ca and Mg originated from the dairy cow diet input for satisfying nutrient requirement of milk production (NRC, 2001). Heat treatment reduced biomass, correspondingly increasing concentrations of P, Ca, and Mg in the BC. For example, average P was significantly increased from 0.91% at 100 °C to 2.66% at 500 °C (Table 1).

Unlike their total concentrations (Table 1), water soluble P, Ca, and Mg in BC for all manures increased as production temperature increased from 25 to 200 °C and then decreased at 200 °C and at 500 °C to levels even below those in the original manure (Fig. 2a, b, and c). The similar concentration trends with heat treatments may be due to association of P–Ca–Mg in the source manures (Josan, 2007). Increase of the water solubility in the BC produced at slightly elevated temperatures ($\leqslant$200 °C) could be explained by total P increase due to biomass reduction. When temperature was further increased (e.g., 500 °C), amorphous P–Ca–Mg could crystallize to form less soluble phases at 500 °C. High P in all BC, especially highest water soluble P (approximately 1500–2700 mg kg^{-1}) at 200 °C indicated that dairy manure-derived BC may become a potential P resource for retaining heavy metals because P tends to react with metals to form insoluble metal phosphate minerals (e.g., pyromorphite $Pb_5(PO_4)_3Cl$, Ksp approximately 10^{-80}) (Cao et al., 2002). However, low solubility of P at 350 and 500 °C may allow these BCs to be a slow P release fertilizer for improving crop production while limiting leaching of excessive P from direct use of raw manure (Harris et al., 2008).

Soluble NH_4–N in the BC for all manures consistently decreased with increasing temperature (Fig. 2d). The decrease in NH_4–N was attributed to the removal of N via volatilization during the heat treatment. Furthermore, the N-containing structures in the BC, such as amino acids, amines, and amino sugars during the high-temperature treatment (500 °C) process were probably condensed to form N-heterocyclic aromatic structures. Thus, much of the residual N in the BC was likely present as recalcitrant heterocyclic N rather than the more available amine N. The NH_4–N is one parameter that is used in evaluating the potential of a material to be used as a soil amendment. Therefore, it is better to carbonize the manure at a relatively low temperature (less than 200 °C) than at higher temperatures in order to utilize the NH_4–N content of the sample for crop nutrition purposes.

3.4. XRD

Since physico-chemical properties of BC for all four manures were similar, we anticipated that the solid components would also be similar. Thus, BC derived from one manure, M-3, was selected for solid component characterization using XRD, TG, and FTIR. In the XRD analysis, BC25 showed elevated background between $2\theta = 14$ to 26°, likely attributable mainly to organic matter

Table 1
Concentrations of the concerned elements of the original manure (BC25) and manure-derived biochar (BC100–BC500) produced at temperatures from 100 to 500 °C.

	Temperature (°C)	C (%)	N (%)	P (%)	Ca (%)	Mg (%)
BC25	25	35.3 ± 5.2a[a]	3.19 ± 0.4a	0.86 ± 0.2c	3.12 ± 0.5c	0.96 ± 0.1c
BC100	100	36.8 ± 4.8a	3.12 ± 0.5a	0.91 ± 0.2c	3.23 ± 0.6c	1.11 ± 0.2c
BC200	200	31.1 ± 3.9a	2.98 ± 0.4a	1.74 ± 0.3b	6.09 ± 0.4b	1.68 ± 0.3b
BC350	350	25.2 ± 2.8b	2.22 ± 0.3b	2.41 ± 0.3a	8.89 ± 1.1a	2.65 ± 0.2a
BC500	500	1.67 ± 0.4c	0.04 ± 0.01c	2.66 ± 0.3a	9.75 ± 1.3a	3.02 ± 0.4a

[a] Mean of four manure samples with standard deviation ($n = 3$ for each manure and $n = 12$ for all four manures). The same letter following the data within the same column indicates no significant difference at $p < 0.05$.

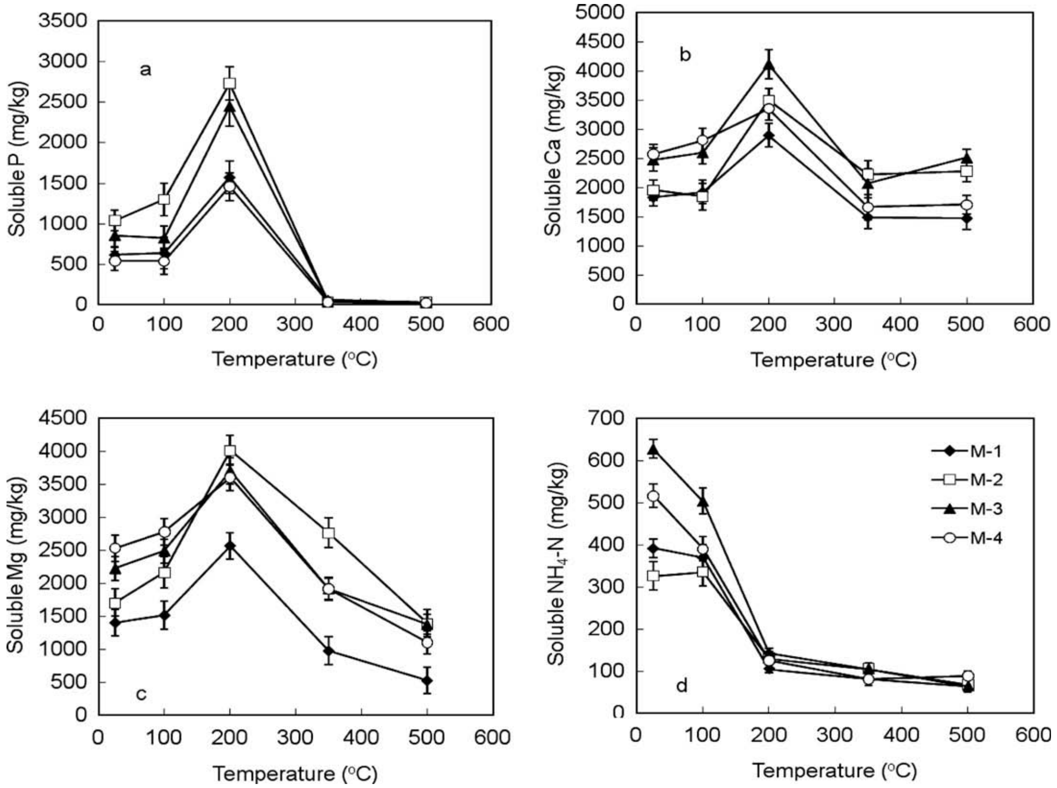

Fig. 2. Concentrations of water soluble P (a), Ca (b), Mg (c), and NH_4–N (d) of all four original manures and manure-derived biochar as a function of production temperatures.

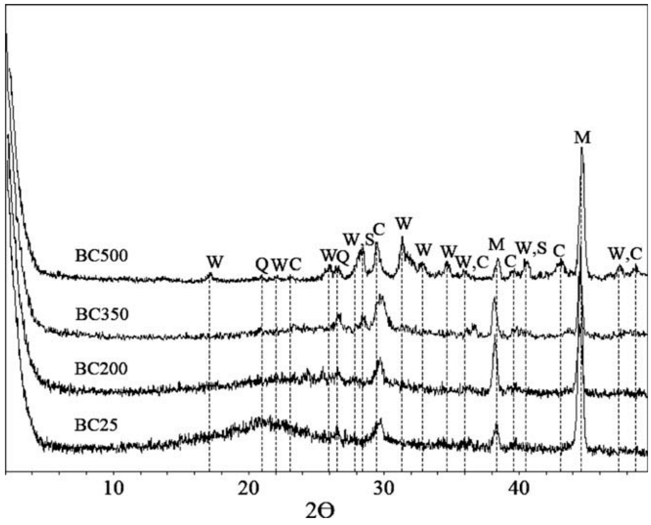

Fig. 3. XRD patterns of the M-3 original manure (BC25) and manure-derived biochar (BC100–BC500) prepared at temperatures from 100 to 500 °C. C, calcite; W, whitlockite; Q, quartz; S, sylvite; M, X-ray mount.

(Fig. 3). The peaks at d = 3.34 and 3.03 Å indicated presence of quartz and calcite, respectively (Fig. 3). The presence of calcite is consistent with the alkalinity of the manure (Fig. 1d). Organic matter combustion with heat resulted in attenuation (BC200 and BC350) or elimination (BC500) of the elevated background (Fig. 3). In addition to calcite and quartz which were present for all BC treatments, sylvite (KCl) was evident in BC350 and BC500. The phosphate mineral whitlockite ($(Ca,Mg)_3(PO_4)_2$) was identified in BC500 (Fig. 3). Whitlockite apparently crystallized with heat, suggesting a stoichiometrically similar noncrystalline precursor; dairy manure commonly contains high levels of P, Ca, and Mg (NRC, 2001). Whitlockite was also found in dairy manure ash by Herrera et al., 2010. Using scanning electron microscopy, Josan (2007) found that P was associated with Ca and Mg in an amorphous form in the manure. Formation of whitlockite in BC500 is consistent with reduction of water soluble P, Ca, and Mg (Fig. 2a, b, and c) in spite of the highest total concentrations for these elements (Table 1).

3.5. TG

Mass loss at temperature up to 180 °C (Fig. 4) likely resulted from sorbed water volatilization. At least some of this water did not readsorb under ambient conditions as evidenced by decreased

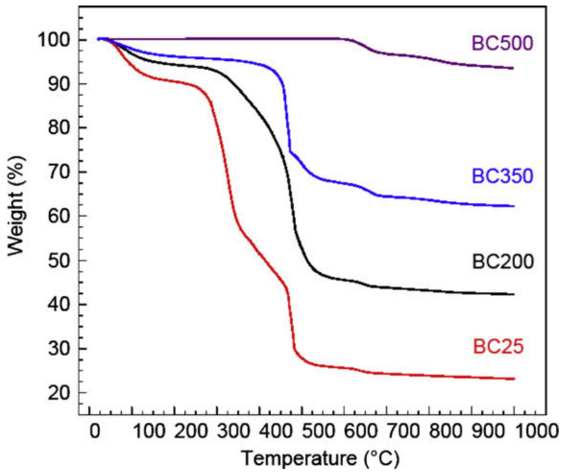

Fig. 4. TG analysis of the M-3 original manure (BC25) and manure-derived biochar (BC100–BC500) prepared at temperatures from 100 to 500 °C.

water loss with increasing BC production temperature (Fig. 4). Higher water in the BC25 may relate to higher porosity attributable to the unaltered organic matter. Mass loss between 200 and 580 °C for BC25, BC200, and BC350 resulted from combustion of organic matter remaining in the BC (Fig. 4); organic matter was essentially depleted in the BC500 due to combustion. The mass loss of organic matter significantly decreased from 64% in BC25 to 0.2% in BC500 (Table 2). In all BC, there was a mass loss occurring between 580 and 740 °C which was attributed to decomposition of calcite. Mass percentages of calcite increased from 2.9% in BC25 to 8.3% in BC500 based on TG weight loss ($CaCO_3 \rightarrow CaO$) due to the mass loss from volatilization of other components.

3.6. FTIR

Differences in infrared spectra reflected water loss, organic matter combustion, and a concentration of mineral components that resulted from those heat-induced mass losses. The spectrum of BC25 was characterized by the organic function groups (Carrizosa et al., 2004; Chen et al., 2008), showing a band from –OH stretching (3294 cm^{-1}), CH_2 (2851 and 2919 cm^{-1}) in biopolymers, C=O stretching of aromatic rings (1593 cm^{-1}) and carboxylic bonds (1711 cm^{-1}), C=C stretching (1275 cm^{-1}), and phenolic-OH stretching (1236 cm^{-1}) (Fig. 5). These bands expectedly decreased with increasing heat (Fig. 5). Bands associated with PO_4^{3-} (1059 cm^{-1}) and CO_3^{2-} (1422 cm^{-1}) increased as a consequence of water and organic matter depletion. Elevating temperature may enhance crystallization of PO_4^{3-}- and CO_3^{2-}- associated minerals, resulting in their peaks resolving into 1097 and 1059 cm^{-1} for PO_4^{3-} and 1487 and 1422 cm^{-1} for CO_3^{2-} in the BC350 and BC500 (Fig. 3). PO_4^{3-} and CO_3^{2-} dominated in BC500, agreeing with the results of XRD and TG analysis (Figs. 3 and 4).

3.7. Lead and atrazine sorption by BC

As high as 93% of Pb was sorbed by BC100, while BC200 and BC350 almost completely (approximately 100%) removed Pb from solution (Table 3). The high Pb sorption capacity is not likely the sole result of surface adsorption considering the low surface area of the BC (Fig. 1c). It may be attributed to precipitation with phosphate due to high P content of BC (Table 1 and Fig. 2a). Phosphate would react with Pb to form stable Pb phosphate minerals (Cao et al., 2002). Our previous work demonstrated precipitation of β-$Pb_9(PO_4)_6$ in BC200 after reaction with aqueous Pb; while higher alkalinity (pH ~10) and calcite (Figs. 1 and 3) in BC350 would allow for precipitation of hydrocerussite $Pb_3(CO_3)_2(OH)_2$ in addition to formation of β-$Pb_9(PO_4)_6$ (Cao et al., 2009).

The BC was also effective in sorbing atrazine. Among three BCs, BC200 was the most effective, with sorption of 77% atrazine (Table 3). Atrazine partitioning into the organic phase was expected to dominate atrazine sorption (Cao et al., 2009). Partitioning of atrazine is positively related to organic C content. Relatively lower sorption by BC350 was probably because of less organic C content (Table 1). In spite of highest C (37%) in BC100, however, this treat-

Table 2
A summary of TG analysis results for the original manure (BC25) and manure-derived biochar (BC200–BC500) prepared at temperatures from 200 to 500 °C.

	Organic matter		$CaCO_3$	
	Temperature range (°C)	Mass loss (%)	Temperature range (°C)	Mass loss (%)
BC 25	202–543	64.3 ± 6.7a[a]	594–681	2.9 ± 0.1d
BC200	211–573	48.2 ± 4.3b	588–682	4.0 ± 0.4c
BC350	236–579	28.2 ± 3.8c	603–726	7.0 ± 0.6b
BC500	223–550	0.10 ± 0.02d	580–736	8.3 ± 0.9a

[a] Mean of four manure samples with standard deviation ($n = 3$ for each manure and $n = 12$ for all four manures). The same letter following the data within the same column indicates no significant difference at $p < 0.05$.

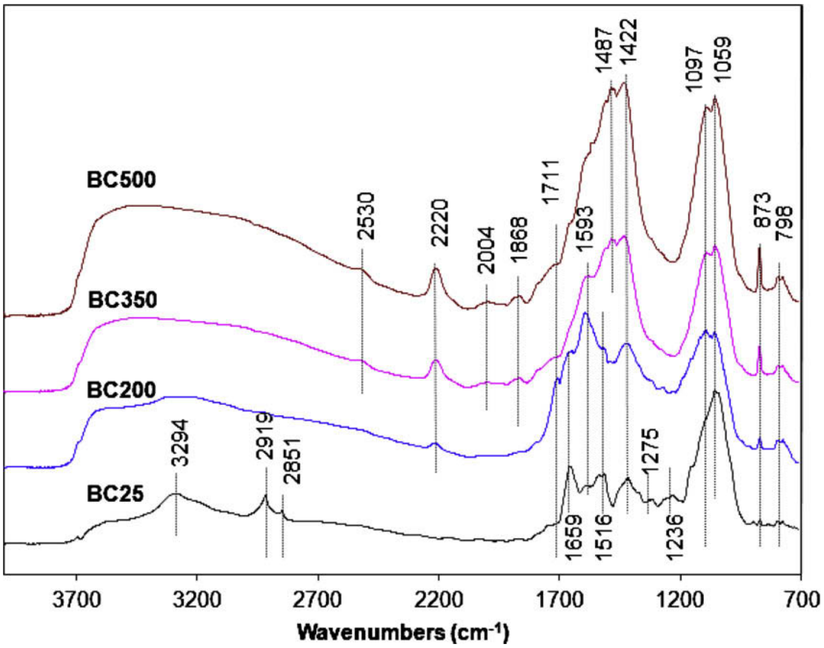

Fig. 5. FTIR spectra of the M-3 original manure (BC25) and manure-derived biochar (BC100–BC500) prepared at temperatures from 100 to 500 °C.

Table 3
Sorption of Pb and atrazine from solution by M-3 derived biochar.

	Pb			Atrazine		
	Initial (mg L^{-1})	Final (mg L^{-1})	Removal (%)	Before (mg L^{-1})	After (mg L^{-1})	Removal (%)
BC100	207	14.9 ± 0.7a[a]	92.8 ± 2.3b	10	7.23 ± 0.4a	27.7 ± 5.2c
BC200	207	0.55 ± 0.1b	99.8 ± 4.1a	10	2.27 ± 0.2c	77.3 ± 6.8a
BC350	207	0.65 ± 0.1b	99.7 ± 5.7a	10	6.01 ± 0.5b	39.9 ± 4.6b

[a] Mean of three replicates with standard deviation ($n = 3$). The same letter following the data within the same column indicates no significant difference at $p < 0.05$.

ment showed the lowest sorption of atrazine, possibly due to suppression of sorption by high dissolved organic C (Cao et al., 2009).

4. Concluding remarks and environmental significance

Dairy manure can be efficiently converted into a BC material with potential to serve as an amendment for remediation or agronomic purposes. The conversion temperature affects BC properties which in turn affects BC application. Heating at ⩾350 °C in presence of air resulted in partial combustion of manure, producing a substantial amount of ash. As a result, the BCs produced at ⩾350 °C (e.g., BC350, BC500) were characterized by higher pH and high calcite content, making the BC beneficial as an amendment to neutralize soil acidity. Phosphorus solubility could be reduced by heating to ⩾350 °C which would render potential of the BC as a slow P release fertilizer for improving crop production while limiting leaching of excessive P from direct use of raw manure. He et al. (2000) also indicated that a substantial reduction in the P mobility of animal manures may be achievable by directly pyrolyzing the manures.

Heating at ⩽200 °C concentrated soluble P and organic C imparting the great capability of BCs (e.g., BC100, BC200) to adsorb Pb and atrazine from aqueous solutions. Thus, dairy-manure-derived BC has potential to be an effective adsorbent for application in environmental remediation. Overall, turning animal manures into BC for remediation application shows promise as a means to solve disposal problem while creating new markets for animal manures.

Acknowledgements

This research was supported in part by the Foundation of The State Key Laboratory of Pollution Control and Resource Reuse, China (No. PCRRVF09001), National Natural Science Foundation of China (No. 20877056), and University of Florida.

References

Abe, F., 1988. The thermochemical study of forest biomass. Forest. Prod. Chem. 45, 1–95.

Abe, I., Iwasaki, S., Iwata, Y., Kominami, H., Kera, Y., 1998. Relationship between production method and adsorption property of charcoal. TANSO 185, 277–284.

Ahmedna, M., Marshall, W.E., Rao, R.M., 2000. Production of granular activated carbons from select agricultural byproducts and evaluation of their physical, chemical and adsorption properties. Bioresour. Technol. 71, 113–123.

Bergman, P.C.A., Kiel, J.H.A. Torrefaction for biomass upgrading. The 14th European Biomass Conference & Exhibition, Paris, France, 17–21 October 2005.

Cao, X., Ma, L.Q., Chen, M., Singh, S.P., Harris, W.G., 2002. Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. Environ. Sci. Technol. 36, 5296–5304.

Cao, X., Ma, L.Q., Gao, B., Harris, W., 2009. Dairy manure-derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 43, 3285–3291.

Carrizosa, M.J., Koskinen, W.C., Hermosin, M.C., 2004. Interactions of acidic herbicides bentazon and dicamba with organoclays. Soil Sci. Soc. Am. J. 68, 1863–1866.

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137–5143.

Chun, Y., Sheng, G., Chiou, C.T., Xing, B., 2004. Compositions and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655.

Harris, W.G., Wilkie, A.C., Cao, X., Sirengo, R., 2008. Bench-scale recovery of phosphorus from flushed dairy manure wastewater. Bioresour. Technol. 99, 3036–3043.

He, B.J., Zhang, Y., Funk, T.L., Riskowski, G.L., Yin, Y., 2000. Thermochemical conversion of swine manure: an alternative process for waste treatment and renewable energy production. Trans. ASAE 43, 1827–1834.

Herrera, D.H., Harris, W.G., Nair, V.D., Josan, M., Staples, C.R. 2010. Effect of dietary modifications of calcium and magnesium on reducing solubility of phosphorus in feces from lactating dairy cows. J. Dairy Sci. (in press).

Johns, M.M., Marshall, W.E., Toles, C.A., 1998. Agricultural byproducts as granular activated carbons for adsorbing dissolved metals and organics. J. Chem. Technol. Biotechnol. 71, 131–140.

Joint Committee on Powder Diffraction Standards (JCPDS). 1980. Mineral Powder Diffraction File Search Manual or Data Book. The Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Pennsylvania, USA.

Josan, M.S. 2007. Manure-derived components and their influences on long-term stability of P in soils. Ph.D. Disseration, University of Florida.

Koneswaran, G., Nierenberg, D., 2008. Global farm animal production and global warming: Impacting and mitigating climate change. Environ. Health Perspect. 116, 578–582.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitig. Adapt. Strat. Glob. Change 11, 403–427.

Lehmann, J., 2007a. Bio-energy in the black. Front. Ecol. Environ. 5, 381–387.

Lehmann, J., 2007b. A handful of carbon. Nature 447, 143–144.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation exchange capacity in soils. Soil Sci. Soc. Am. J. 70, 1719–1730.

Lima, I.M., Marshall, W.E., 2005a. Granular activated carbons from broiler manure: physical, chemical and adsorptive properties. Bioresour. Technol. 96, 699–706.

Lima, I.M., Marshall, W.E., 2005b. Utilization of turkey manure as granular activated carbon: physical, chemical and adsorptive properties. Waste Manage. 25, 726–732.

Lima, I.M., Marshall, W.E., 2005c. Adsorption of selected environmentally important metals by poultry manure-based granular activated carbons. J. Chem. Technol. Biotechnol. 80, 1054–1061.

Marshall, W.E., Ahmedna, M., Rao, R.M., Johns, M.M., 2000. Granular activated carbons from sugarcane bagasse: production and uses. Int. Sugar J. 102, 1215.

Martins, A.F., Cardoso, A.L., Stahl, J.A., Diniz, J., 2007. Low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent. Bioresour. Technol. 98, 1095–1100.

National Research Council (NRC). 2001. Nutrient Requirements of Dairy Cattle, seventh ed (rev). National Academy Press, Washington, DC.

Ng, C., Losso, J.N., Marshall, W.E., Rao, R.M., 2002. Physical and chemical properties of selected agricultural byproduct-based activated carbons and their ability to absorb geosmin. Bioresour. Technol. 84, 177–185.

Olsen, S.R., Sommers, L.E. 1982. Phosphorus. In: Page et al. A.L. (Eds.), Methods of Soil Analyses: Part 2 Chemical and Microbiological Properties, Am. Soc. Agron., WI, USA, pp. 403–430.

Renner, R., 2007. Rethinking biochar. Environ. Sci. Technol. 41, 5932–5933.

Sharpley, A., Foy, B., Withers, P., 2000. Practical and innovative measures for the control of agricultural phosphorus losses to water: an overview. J. Environ. Qual. 29, 1–9.

Shinogi, Y., Kanri, Y., 2003. Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. Bioresour. Technol. 90, 241–247.

Shinogi, Y., Yoshida, H., Koizumi, T., Yamaoka, M., Saito, T., 2003. Basic characteristics of low-temperature carbon products from waste sludge. Adv. Environ. Res. 7, 661–665.

Sumiyaki Association. 1991. Charcoal and wooden acid liquid. Ienohikari Association (in Japanese).

Toles, C.A., Marshall, W.E., Johns, M.M., 1997. Granular activated carbons from nutshells for the uptake of metals and organic compounds. Carbon 35, 1407–1414.

US Environmental Protection Agency (USEPA). 1986. Test methods for evaluating solid waste, Laboratory Manual Physical/Chemical Methods, US Gov. Print Office, Washington, DC.

Zhang, H., Dao, T.H., Basta, N.T., Dayton, E.A., Daniel, T.C. 2006. In: Rice, J.M., Caldwell, D.F., Humenik, F.J. (Eds.), Remediation and techniques for manure nutrient loaded soils. 161–180 in Animal Agriculture and the Environment: National Center for Manure and Animal Waste Management White Papers. St. Joseph, Michigan: ASABE, pp. 482–504.